Unusual vortex structure in ultrathin $Pb(Zr_{0.5}Ti_{0.5})O_3$ films

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Using a first-principles-based approach, we determine the ferroelectric pattern in $PbZr_{0.5}Ti_{0.5}O_3$ ultrathin film. It is found that vortex stripes are formed in the system and they are responsible for the 180° domains observed. When a local external field is exerted, the vortex stripe transforms into the vortex loop structure, which leads to the formation of a smaller domain with the polarization antiparallel to the field in the center of the field region. This may provide a convenient way to manipulate nanodomains in thin films.

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During the past decade, the extensive research on ferroelectric thin films has been carried out not only due to their promising applications in microelectronics such as nonvolatile random access memories [1, 2, 3] but also due to their novel physical properties. Ferroelectricity is a collective phenomenon resulting from the delicate balance between the long-range dipole interaction and short-range covalent interaction. In nanostructures such as ultrathin films, both long-range dipole and short-range covalent interactions and their balance are varied in regard to those in the bulk. Therefore, it is commonly believed that the nanostructure will have some physical properties distinctly different from those of bulk materials, e.g., the size effects that the ferroelectricity would disappear below a critical size[4, 5, 6, 7, 8, 9]. Recently, an unusual atomic off-center displacements vortex pattern in $BaTiO_3$ nanodot was revealed in simulation[10]. In ferroelectric ultrathin films, the periodic 180° stripe domains have been observed with X-ray study [5, 11] and simulated using a first-principles based approach[8, 12, 13].

Generally, the ferroelectric nanodomain is read or written with a metallic tip of some kinds of microscope such as atomic force microscope. Therefore, it is important to clarify how the ferroelectric pattern of ultrathin films is influenced by the local field produced by the tip. Herein, we conducted a first-principles-based computer simulation to investigate this problem. It is found that a polarization vortex loop is induced under a local external field, and the polarizations in the center of the field region are antiparallel with the field. This unusual phenomenon may be helpful in manipulating the nano-structure in the ultrathin film.

The system we investigated is the disorder $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT) thin films. We adopt the effective Hamiltonian of PZT alloys proposed by Bellaiche, Garcia and Vanderbilt [14], which is derived from first-principles calculations, to predict the properties of the system by Monte Carlo simulation. The method can provide the microscopic information about the atomic off-center displacements and therefore is especially suitable for investigating the film without any charge screening. In this scheme, the total energy E is written as the sum of an average energy and a local energy as [14, 15]

$$E(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\eta_H,\{\sigma_j\}) = E_{\rm ave}(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\eta_H) + E_{\rm loc}(\{\mathbf{u}_i\},\{\mathbf{v}_i\},\{\sigma_j\}), \quad (1)$$

where $\mathbf{u}_i$ is the local soft mode in the i-th unit cell and associated with the local electrical dipoles $\mathbf{P}_i = Z^*\mathbf{u}_i$ (where Z^* is the effective charge of the local mode), $\mathbf{v}_i$ is the dimensionless local displacement[16], η_H is the homogeneous strain tensors and $\sigma_j = \pm 1$ represents the presence of a Zr or Ti atom at the j-th lattice site. All the parameters of the Hamiltonian are derived from the first principle calculations and are given in references [14, 15]. In our simulations, we do not include the external term of surface effect proposed by Fu and Bellaiche while simulating nanoscopic structures, since they have demonstrated that the term has almost no effect on the polarization pattern[10, 17]. The fact that the calculated critical thickness[8] is well consistent with the X-ray study[5] further justifies our above treatment.

PZT film is surrounded by vacuum. To efficiently calculate the long-range dipole-dipole interaction energy in thin films which lack the periodicity in the out-of-plane direction, we adopt the corrected three-dimensional Eward method, whose validity has been verified analytically by Bródka and Grzybowski [18]. In that scheme, a small empty space (about three times of the film thickness) introduced in the simulation box to surround the film can lead to very well converged results. The z axis ([001] direction) is taken along the growth direction of the film, and the x and y axes are chosen to be along the pseudocubic [100] and [010] directions. The influence of the substrate is imposed by confining the homogeneous in-plane strain. Namely, $\eta_1 = \eta_2 = 2\%$ and $\eta_6 = 0$. The temperature of the simulation is 50 K, corresponding to a rescaled experimental temperature of 30 K[14].

We first investigate in detail the polarization pattern in the ultrathin film under zero field, which is helpful for clarifying the effect of local electric field. Our previous

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work demonstrated the existence of the periodic out-of-plane 180° stripe domains in the films under 2% compressive strain[8]. Now we further find that the stripes exhibit unusual microscopic structures. An example of a $15 \times 15 \times 4$ supercell is given in Fig. 1. A special vortex structure can be clearly observed on the $x - z$ plane [Fig. 1(a)]. The clockwise and anticlockwise vortex appear alternately. This vortex structure extends along the y axis as vortex stripe. One of the outcomes of the vortex stripe is that the local mode perpendicular to the stripe, u_x, also forms the stripe structure in each $x-y$ plane [see Fig. 1(b) for $z = 1$ plane]. The average effect of vortex structures directly result in 180° out-of-plane polarization stripe domains. The out-of-plane polarization stripe domain wall is located at the center of vortex. Therefore each out-of-plane polarization domain does not superpose with the vortex stripe but strides across two neighboring vortex stripes. The film thickness and the stripe width just denote two characteristic sizes of the vortex. Then we can understand intuitively why the stripe domain period increases with the film thickness, since the vortex expands with increasing film thickness. While the film thickness is of 4 unit cell (1.6 nm), the simulated stripe period is 2.8 nm, which is quantitatively well consistent with the experimental measurement[11].

The above vortex structure comes from the delicate balance between the long-range dipole interaction and short-range covalent interaction. For the dipole-dipole interaction, the alignment of head to end is favorable in energy, while the head to head is unfavorable. Due to the existence of the vacuum and the absence of the screening effect, the surface dipoles tend to align parallel with the surface to stabilize the dipole-dipole interaction. The short-range covalent interaction supports the dipoles to change smoothly. In the internal layers, because of the large compressive strain, the local mode tends to align along the normal direction. The vortex structure meet all the above demand, and, with periodical arrangement, effectively eliminate the depolarization field.

Now we turn our attention to the influence of the local field on the microscopic structure. In our simulation, the local field produced by the tip is assumed to exert in a smaller region, $N_E \times N_E \times 4$, of the supercell. Due to the periodic boundary condition adopted in the film plane, the local field will appear periodically, which is similar to the field created by the array of the tips. Generally, we can expect that a ferroelectric nanodomain will be formed when a local field is exerted. However, to our surprise, the actual situation is not so simple. Fig. 2 depicts the out-of-plane local mode (namely polarization) of the film with $E = 2 \times 10^7$ V/m and $N_E = 10$. Although the field aligns most out-of-plane polarizations in the field region along the field direction, the polarizations near the center of the field region are opposite with the field. The smaller region where out-of-plane polarization is antiparallel with the field is approximately round in shape.

More details of the polarization pattern are given in Fig. 3. Although the clockwise and anticlockwise vortexes still appear alternately in the $x-z$ plane [Fig. 3(a)], the straight stripe in the $x - y$ plane is destroyed by the local field and a vortex loop appears in the field region as shown in Fig. 3(b). Our detailed analysis shows that the vortex loop structure could be regarded as being formed by the rotation of the inner vortex around the oo' axis [Fig. 3(a)]. Fig. 3(b) supports this conclusion by means of the facts that the boundary line between the inner vortex and the outer vortex is roughly round (the dashed circle in the graphics) and the local modes inside the circle are almost radialized. Similar proof is also observed in Fig. 2. Therefore, our simulations demonstrate that the local field can result in the transformation of the vortex straight stripe into the vortex loop.

The above unusual phenomena are closely related with the character of the stripe. On the one hand, the shape of vortex is rather stable. The stripe width is determined

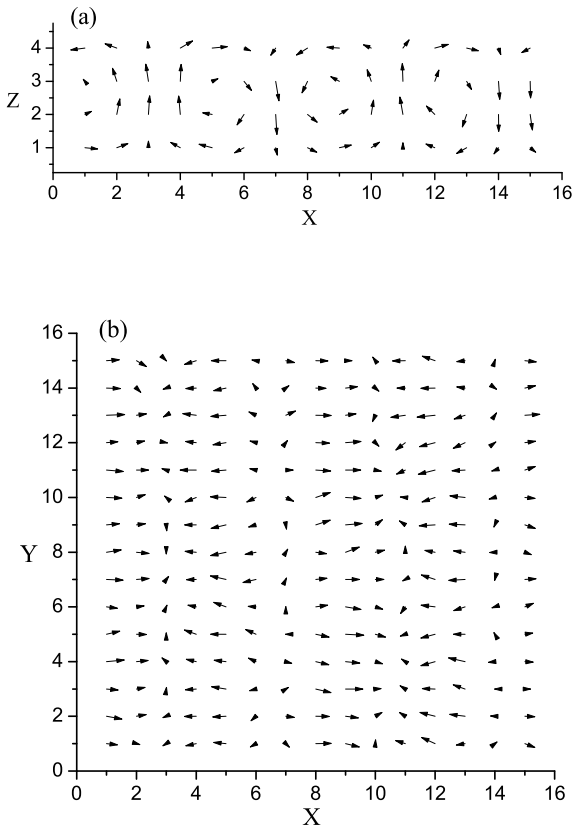

FIG. 1: Local-mode displacement, $\mathbf{u}_i$, of the cell in (a) $y = 8$ plane, (b) $z = 1$ plane of $15 \times 15 \times 4$ supercell. The arrows give the directions of these displacements, projected on corresponding planes and the arrow length indicates the projected magnitude.

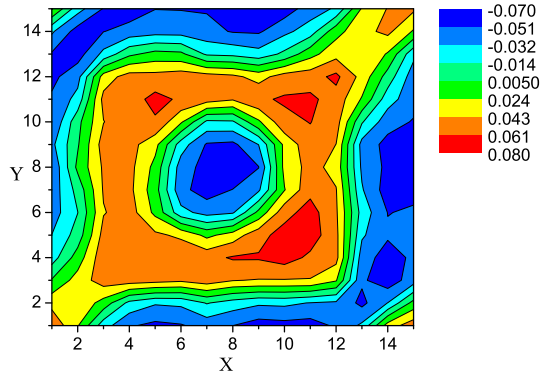

FIG. 2: (color online) The out-of-plane local modes of $15 \times 15 \times 4$ supercell. A local field $E = 2 \times 10^7$ V/m is exerted on a smaller region of $10 \times 10 \times 4$ (namely $N_E = 10$).

only by the film thickness and it is almost independent of the temperature and compressive strain until the stripe disappears. The influence of the global external field (i.e., the field is exerted on the whole supercell) on the stripe width is also considerably small. Our simulations indicate that the stripe width does not alter appreciably after applying a very large external field (10^8 V/m) to the supercell. All of these results clearly demonstrate that the shape of vortex is very stable. On the other hand, the stripe structure composed of the vortex is considerably flexible. Our simulations show that besides the straight stripe mentioned above, many kinds of bent stripes also correspond to local minimum of the energy. Although the internal energy of these bent stripes are larger than that of the straight stripe, the energy difference is very small. Therefore we can conveniently trap some bent stripe by applying and removing the local field with different configuration. For example, similar vortex loop structure with Fig. 2 can be trapped when applying and then removing the local field. The corresponding internal energy is larger than that of the straight stripe by only about 1 meV /5 atoms. The diameter of the inner domain in the vortex loop structure is smaller than the stripe period τ ($\tau \approx 7$ in the current case). Therefore, when N_E (denoting the field region of the external local field) exceeds τ, no configuration of polarization can make the whole field region occupied by the parallel phase. Alternately, a loop structure with antiparallel polarization in the center, as that in Figs. 2 and 3, is the optimum scheme to have as much parallel polarization as possible in the action range of the local field. It is the reason of the appearance of the central antiparallel domain. When the external field range N_E further increases, the number of the loop stripe in the structure will increase due to the fact that the width of the loop stripe is almost fixed, and a parallel domain (data not shown) may appear in the center.

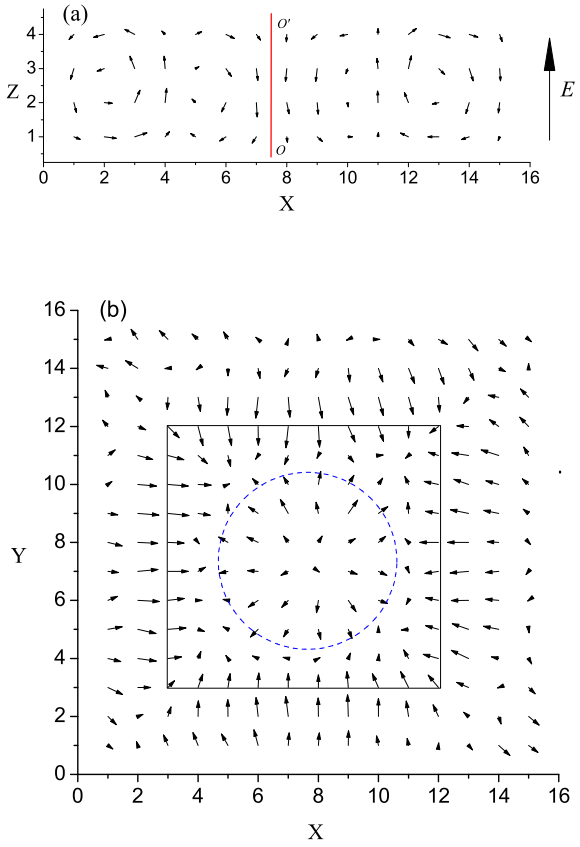

FIG. 3: Local-mode displacements, $\mathbf{u}_i$, of the cell in (a) $y = 8$ plane, (b) $z = 1$ plane of $15 \times 15 \times 4$ supercell. The arrows give the directions of these displacements, projected on corresponding planes and the arrow length indicates the projected magnitude. A local field $E = 2 \times 10^7$ V/m along the z axis is exerted on a smaller region $10 \times 10 \times 4$ denoted by solid line. The dash line shows the boundary of the inner vortex and the outer vortex.

Our simulations indicate that the same phenomena also appear in thicker films (such as the films with the thickness of 6 and 8 unit-cells). Furthermore, the radius of central anti-parallel domain is only determined by the film thickness. The influence of the size of the field region and in-plane size of the supercell on the radius of anti-parallel domain could be overlooked. The radius of anti-parallel domain is a little larger than half of the stripe width, and is much smaller than the size of the field region (denoted by N_E). Therefore, our results imply that we can write a naondomain whose size is far smaller than the radius of tip. This unique character may have potential application in improving the storage densities of ferroelectric memory. In general, in order to improve the storage density, we need to decrease the radius of the tip since the size of tip is a very important factor to determine the lower limits of the radius of nanodomain. However, it is obvious that decreasing of

the tip radius has its own limit below which it would be very difficult to further reduce the tip. Our simulation suggests a possible approach to break through the limit imposed by the radius of tip. According to our calculated results and the fact that the stripe width of the 100-nm-thick $PbTiO_3$ film is about 10 nm by X-ray study [11], we can estimate that the radius of anti-parallel domain in an 100-nm-thick $PbTiO_3$ film is about 5 nm, corresponding to a considerably small dot.

It should be noted that the formation of the vortex structure such as the vortex stripe and loop is closely related with the electric boundary condition adopted in our simulations (i.e., no surface charge induced by polarization is screened). With enhancing screening of surface charges, the vortex stripe domains will transform into monodomain[12]. In fact, the perfect screening is not achieved even under short circuit boundary conditions in ultrathin film. For example, a sizeable depolarization field is quantified by Junquera and Ghosez[9] through the first principles calculation. Such a field was recently suggested to explain experimental changes of the coercive fields with the film thickness[19]. The effect of the screening became weaker when the top electrode has been replaced by the metallic tip, which is just the case of writing the nanodomain in ferroelectric films. A larger depolarization field will be formed in those ferroelectric films. Therefore, the phenomena that the direction of the polarization is antiparallel with the field near the center of the field region will be promisingly observed in perovskite ferroelectric film.

Similar anti-parallel poling reversal phenomenon has been reported by Abplanalp *et al.*[20] and Morita *et al.*[21]. However, this phenomenon is not induced by the depolarization field, and has different microscopic origin from ours. In Abplanalp *et al.*'s study[20], the anti-parallel reversal is ferroelastoelectric switching and is achieved in $BaTiO_3$ thin film by simultaneously applying electric field and compressive stress with the tip of a scanning force microscope. In Morita *et al.*'s study[21], the depolarization field should be small since the film can be poled into monodomain. Although the reason of anti-parallel poling reversal is still unclear, it is suggested that this phenomenon is related to the mechanical force imposed by the tip. Furthermore, the anti-parallel poling appears only after the electric field is removed, which is different from our results that the anti-parallel polarization starts to appear under the local field.

In summary, the ferroelectricity of ultrathin PZT films without any charge screening has been investigated with the Monte Carlo simulations based on a first-principles-derived Hamiltonian. The off-center displacement in the film exhibits vortex stripes with unusual characters. On the one hand, the shape of vortex is rather stable. On the other hand, the stripe structure composed of the vortex is considerably flexible and can be easily manipulated. The unusual characters of the vortex stripe lead to an interesting phenomenon. The local field can transform the vortex straight stripe into the vortex loop structure, which results in the formation of a round-shape domain with the polarization antiparallel with the field near the center of the field region. The area of the anti-parallel domain is much smaller than the area of the field region. This implies a way to write a very small nanodomain with the general tip, which might have some potential application in improving the storage densities of ferroelectric memory.

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